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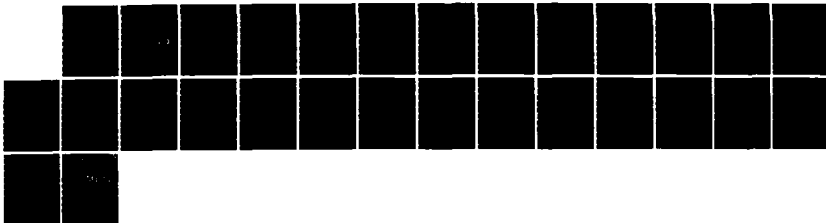
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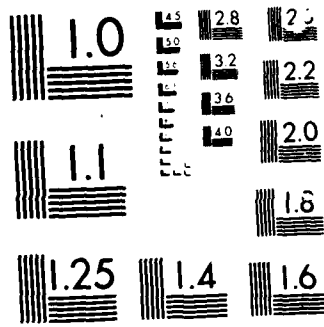
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## 20. ABSTRACT CONTINUED

Photoluminescence spectra and lifetimes has been measured in ordered-perovskite ( $\text{Cs}_2\text{NaYCl}_6$ ,  $\text{K}_2\text{NaScF}_6$  and  $\text{K}_2\text{NaGaF}_6$ ) low-crystal-field host crystals. After the failure of linear-coupling models was demonstrated, a successful theoretical model was proposed in which fluorescence quenching is mediated by quadratic coupling to assymmetric modes of vibration. Parameters of the model are constrained by empirical spectral information, and radiationless transition rates are calculated by numerical line-shape simulation. Both semi-empirical (INDO) and ab-initio molecular-orbital cluster calculations have been performed in conjunction with lattice-statics calculations in a continuing effort to refine this quenching model. Photoluminescence spectra and lifetimes, measured as functions of temperature and pressure in a diamond-anvil cell, revealed a pressure-induced transition from broad-band fluorescence to narrow-band phosphorescence; i.e., from low-crystal-field to high-crystal-field behavior.

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RADIATIONLESS DEACTIVATION OF LOW-FIELD CHROMIUM COMPLEXES IN SOLIDS

FINAL TECHNICAL REPORT

Ralph H. Bartram

February 20, 1986

U.S. Army Research Office

Contract No. DAAG29-82-K-0158

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## ABSTRACT

Thermal quenching of fluorescence is a major loss mechanism which may impede the performance of tunable solid-state lasers, but whose impact is difficult to assess a-priori. The object of the reported investigation was to achieve a quantitative understanding of the factors which control this process, with the ultimate goal of formulating design criteria for tunable solid-state laser materials. The temperature dependence of chromium photoluminescence spectra and lifetimes has been measured in ordered-perovskite ( $\text{Cs}_2\text{NaYCl}_6$ ,  $\text{K}_2\text{NaScF}_6$  and  $\text{K}_2\text{NaGaF}_6$ ) low-crystal-field host crystals. After the failure of linear-coupling models was demonstrated, a successful theoretical model was proposed in which fluorescence quenching is mediated by quadratic coupling to asymmetric modes of vibration. Parameters of the model are constrained by empirical spectral information, and radiationless transition rates are calculated by numerical line-shape simulation. Both semi-empirical (INDO) and ab-initio molecular-orbital cluster calculations have been performed in conjunction with lattice-statics calculations in a continuing effort to refine this quenching model. Photoluminescence spectra and lifetimes, measured as functions of temperature and pressure in a diamond-anvil cell, revealed a pressure-induced transition from broad-band fluorescence to narrow-band phosphorescence; i.e., from low-crystal-field to high-crystal-field behavior.

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## STATEMENT OF PROBLEM STUDIED

The theory of radiationless transitions is well understood in principle, but there is a paucity of examples of its detailed quantitative application to well characterized systems, especially in the intermediate-coupling regime occupied by transition-metal complexes. The aggressive extension of theory has been made urgently imperative by the exploitation of such systems in tunable-laser materials, where thermal quenching of fluorescence is a major loss mechanism whose impact is difficult to predict. The reported investigation was initiated with the object of achieving some quantitative understanding of the factors which control this process. The ultimate goal is to develop theoretical models with genuine predictive capability, in order to provide guidance in the selection of potential tunable-laser materials by permitting their a-priori evaluation with respect to this loss mechanism.

A coordinated theoretical and experimental investigation of radiationless transitions of low-field chromium complexes in ordered perovskites was conducted. Photoluminescence spectra and lifetimes were measured as functions of temperature, in order to characterize the complexes and to extract activation energies for thermal quenching of fluorescence. Several theoretical models for radiationless deactivation, with parameters severely constrained by empirical spectral information, were investigated by numerical line-shape simulations. Photoluminescence spectra were measured as functions of temperature and pressure in a diamond-anvil cell. Semi-empirical molecular-orbital cluster calculations were initiated.

## SUMMARY OF RESULTS

## I. Introduction

Low-crystal-field octahedral complexes of  $\text{Cr}^{3+}$  are characterized by broad-band ( ${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$ ) fluorescence, in contrast with high-field complexes which exhibit narrow-band ( ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ ) phosphorescence (Fig. 1).<sup>1</sup> This property, together with a large Stokes shift, make these low-field complexes ideal candidates for tunable solid-state vibronic laser applications. Examples of host crystals for chromium-based vibronic lasers include alexandrite,<sup>2</sup> emerald<sup>3</sup> and gadolinium-gallium garnet.<sup>4</sup> However, the strong electron-lattice coupling which lends useful properties to these and analogous materials, such as octahedral complexes of  $\text{V}^{2+}$ ,<sup>5</sup> also enhances their susceptibility to thermal quenching of fluorescence.

The project reported here involved an investigation of thermal fluorescence quenching in low-field chromium complexes in ordered perovskites (elpasolites). This class of host materials possesses the virtue that a trivalent cation impurity can be accommodated in a rigorously octahedral site without charge compensation. Additionally, it provides chemical sequences with a range of lattice parameters and crystal fields. Fluorescence spectra and lifetimes have been measured as functions of temperature in order to parametrize models and to determine activation energies and pre-exponential frequency factors for radiationless transition rates. We have proposed a theoretical model for fluorescence quenching<sup>6</sup> in which two electronic states are coupled to two modes of vibration. In this model, radiationless deactivation of the chromium complex is mediated by quadratic coupling to an asymmetric mode. It has also been established that postulated promoting-mode selection rules<sup>7</sup> are ineffectual in these compounds. A systematic investigation of the effects of hydrostatic pressure on these systems is in progress. Photoluminescence spectra measured in

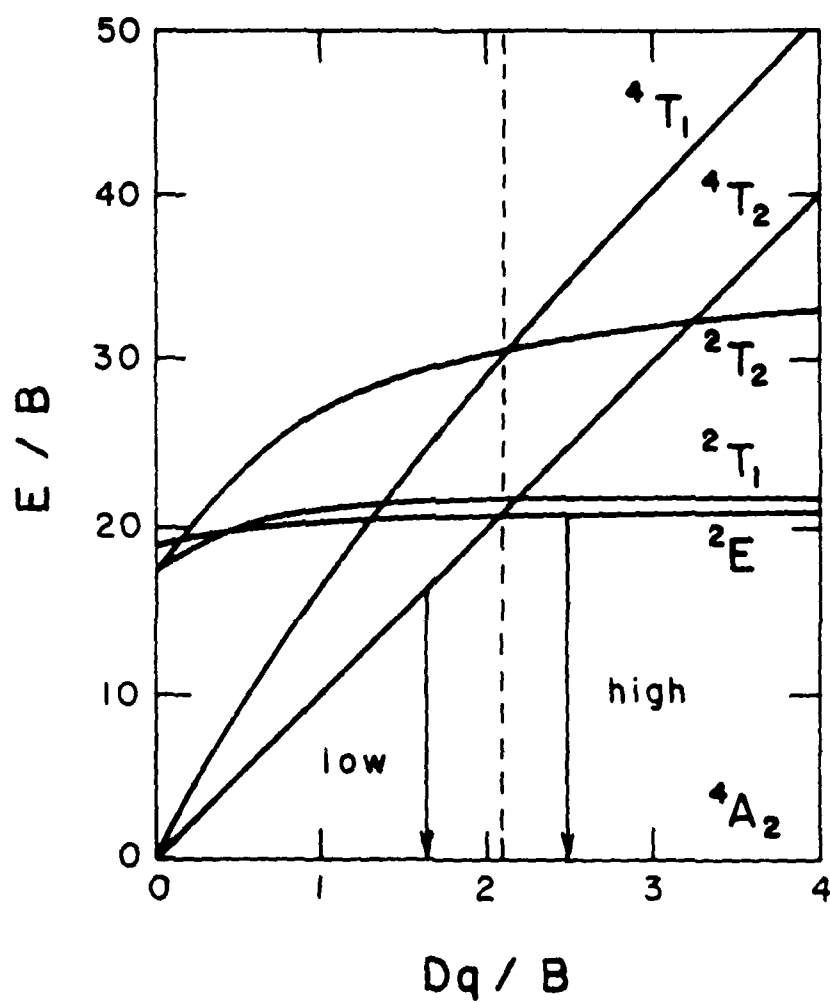


Fig. 1. Tanabe-Sugano energy-level diagram for octahedral chromium complexes.

a diamond-anvil cell as a function of both temperature and pressure reveal a transition from low-field to high-field behavior. Calculations in progress permit simulation of pressure effects through lattice-parameter variation.

Photoluminescence measurements in the diamond-anvil cell will be extended to encompass pressure and temperature dependence of excitation spectra and fluorescence lifetimes as well as fluorescence spectra. These measurements will permit correlation of changes in the activation energy for fluorescence quenching with shifts in energy levels accompanying reduction of lattice parameter, and thus provide a critical test of the theoretical model for radiationless deactivation.

## II. Theoretical Background

There exists an extensive literature on the theory of radiationless transitions spanning the thirty-five years that have elapsed since the pioneering contributions of Huang and Rhys<sup>8</sup> and Lax.<sup>9</sup> Since no radiationless transitions are possible between exact eigenstates of a physical system, the radiationless transition rate depends on the non-stationary state which is prepared in a given experiment. In the adiabatic-coupling scheme, radiationless transitions are assumed to proceed from Born-Oppenheimer states

$$\psi_{n\mu}(r, Q) = \phi_n(r, Q) \chi_{n\mu}(Q) \quad (1)$$

and are mediated by the non-adiabaticity operator  $H_{NA}$  defined by

$$H_{NA} \psi_{n\mu}(r, Q) = [T_N, \phi_n(r, Q)] \chi_{n\mu}(Q), \quad (2)$$

where  $T_N$  is the nuclear kinetic energy operator. First order time-dependent perturbation theory then leads to an expression for the radiationless transition rate  $W_{NR}$  of the form

$$W_{NR} = v\omega[\bar{n}G(\Omega_0+\omega) + (\bar{n}+1)G(\Omega_0-\omega)]. \quad (3)$$

It is convenient to distinguish between promoting modes, which mix the electronic states, and accepting modes, which absorb their energy difference. Coupling to accepting modes is reflected in the normalized lineshape function  $G(\Omega)$ , where  $\Omega$  is measured from the zero-phonon transition and  $\hbar\Omega_0$  is the energy gap to be spanned in the multi-phonon transition. The promoting-mode interaction is incorporated in the factor  $v\omega$ , where  $\omega$  is the promoting-mode frequency. The phonon occupation number  $\bar{n}$  is given by

$$\bar{n} = [\exp(\hbar\omega/k_B T) - 1]^{-1}. \quad (4)$$

Bixon and Jortner<sup>10</sup> have argued that the commonly adopted adiabatic-coupling scheme is appropriate under a wide range of the circumstances. However, an alternative static-coupling scheme has been advocated as well<sup>11,12</sup>. In this scheme, which is also designated "crude-adiabatic", the electronic wavefunctions  $\phi_n(r)$  are taken to be independent of nuclear coordinates. The non-adiabaticity operator is then ineffectual, and radiationless transitions are mediated instead by off-diagonal elements of the potential-energy operator.

The promoting factor  $v$  has been the topic of recent discussion and controversy. Several investigators have demonstrated the equivalence of adiabatic- and static-coupling schemes at a certain level of approximation, and have discredited the popular "Condon approximation" introduced by Huang and Rhys.<sup>8</sup> The static-coupling scheme provides the most tractable formula for  $v$ :

$$v = (\pi/\hbar^2) |\langle \phi_f(0) | \partial H / \partial Q_p | \phi_i(0) \rangle|^2, \quad (5)$$

where  $Q_p$  is the promoting-mode configuration coordinate.

### III. Application to Low-Field Chromium Complexes in Ordered Perovskites

The theory of radiationless transitions as outlined above was applied to low-field chromium complexes in ordered perovskites in an effort to explain the observed fluorescence quenching, as inferred from the temperature dependence of fluorescence lifetimes shown in Fig. 2.<sup>6</sup> The rapid decline at high temperature is attributed to competing radiationless transitions whose rate can be expressed approximately in the form

$$W_{NR} = S \exp(-\Delta E/k_B T). \quad (6)$$

A promoting mode of  $t_{1g}$  symmetry is required in order to couple the  ${}^4T_{2g}$  excited state with the  ${}^4A_{2g}$  ground state. Counter-rotating displacements of anion octahedra about trivalent and monovalent cations were found to provide a strongly coupled mode of the required symmetry,<sup>15</sup> contrary to earlier speculation concerning promoting-mode selection rules.<sup>7</sup> The promoting-mode factor  $S$ , calculated from Eq. (5) with free-ion chromium d orbitals and the exact nuclear potential for the ligands, is of the order of  $10^{15} \text{ sec}^{-1}$  for all three host crystals. Although the theory of radiationless transitions could be formulated analogously in terms of pseudopotentials and pseudowavefunctions, such a formulation would embody a different set of physical assumptions. Radiationless transitions between Born-Oppenheimer states are manifestations of the failure of the electronic wavefunction to adjust to the instantaneous positions of the nuclei. In the pseudopotential approximation, the frozen cores are assumed to follow the nuclei with no difficulty, and only the valence pseudowavefunctions do not; accordingly, the promoting-mode factor  $S$  is grossly underestimated. This situation, which has been discussed by Bartram and Stoneham,<sup>16</sup> is analogous to the Adrian effect in the calculation of spin-Hamiltonian parameters,<sup>17</sup> and the remedy is the same: It is essential to

Fig. 2. Fluorescence lifetimes vs. temperature for  $\text{Cr}^{3+}$  in  $\text{Cs}_2\text{NaYCl}_6$  ( $\diamond$ ),  $\text{K}_2\text{NaScF}_6$  ( $\triangle$ ) and  $\text{K}_2\text{NaGaF}_6$  ( $\square$ ).

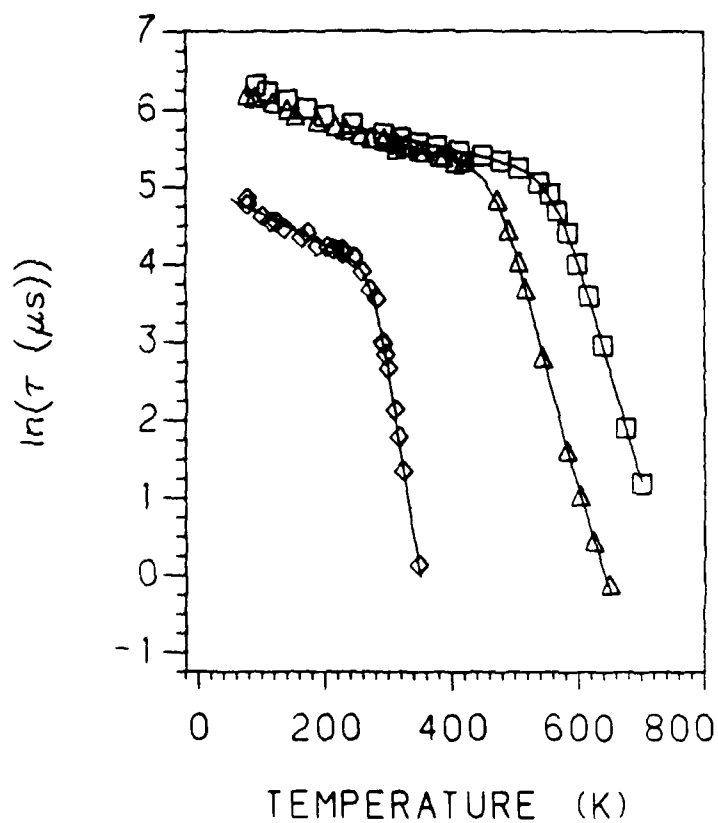
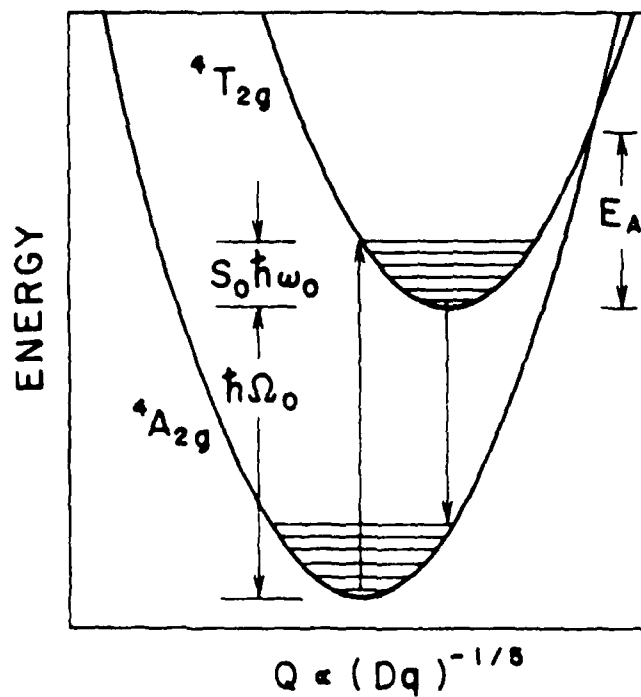


Fig. 3. Single-coordinate, linear-coupling model.



orthogonalize the pseudowavefunctions to ion-core orbitals (in this case occupied ligand orbitals) and to employ the exact Hamiltonian in Eq. (5). Since orthogonalization to ligand core orbitals was not employed in the present work, the calculated values of  $\nu$  should be regarded as preliminary estimates.

The central problem in the application of radiationless-transition theory is evaluation of the normalized lineshape function  $G(\Omega)$  in Eq. (3), which also describes the wavelength dependence of the fluorescence spectrum, for values of its argument which are very far from the range of arguments accessible to direct observation. Values of  $G(\Omega_0 + \omega)$  are extremely sensitive to the precise physical model of the system which is adopted, even when the parameters of the model are constrained by empirical spectral information.

The simplest model considered is based on linear coupling to a single accepting-mode configuration coordinate, which can be identified with a symmetrical ( $a_{1g}$ ) displacement of the ligands. The parameters of this model, defined by Fig. (3), were completely determined by the temperature dependence of the first and second moments of fluorescence spectra, and required values of the lineshape function  $G(\Omega)$  were calculated from the Huang-Rhys formula.<sup>8</sup> The predicted value of the radiationless transition rate  $W_{NR}$  from Eq. (3) was found to be smaller than the experimental value by six-to-eight orders of magnitude with the estimated value of the promoting-mode factor  $\nu = 10^{15} \text{sec}^{-1}$ , although the predicted activation energy was approximately correct. It is evident that this model fails completely to explain the observed thermal quenching of fluorescence. The linear-coupling model was extended to include a range of  $a_{1g}$  vibration frequencies by employing an approximate lineshape theory due to Weissman and Jortner,<sup>18</sup> but this extension failed to yield any improvement.

The failure of linear-coupling models suggested consideration of quadratic coupling; i.e. different vibration frequencies in the two electronic states.



Although quadratic coupling to  $a_{1g}$  modes is possible in principle, it is ruled out in the present system by empirical spectral information. The octahedral chromium complex has additional degrees of freedom, however, and coupling to lower-symmetry accepting modes is permitted by the orbital degeneracy of the  ${}^4T_{2g}$  excited state. A simplified model was considered which includes just two electronic states, the  ${}^4A_{2g}$  state and one orbital component of the  ${}^4T_{2g}$  state, with linear coupling to a single  $a_{1g}$  accepting mode and quadratic coupling to a single  $t_{2g}$  accepting mode. This model is illustrated in Fig. (4). Normalized lineshape functions were calculated for each mode by the method of Struck and Fonger,<sup>19</sup> in which individual vibrational overlap integrals are evaluated by a recursion relation, and the composite lineshape was calculated by numerical convolution. Both the  $a_{1g}$  and ground-state  $t_{2g}$  vibration frequencies were treated as adjustable parameters, but the strength of quadratic coupling was calculated ab-initio from a point-ion model.

Although the number of adjustable parameters is the same as for the multi-frequency linear-coupling model, the two-mode, quadratic-coupling model proved to be far more successful. Not only was it possible to fit the temperature dependence of fluorescence spectra and the activation energy for thermal quenching simultaneously, but the model also yielded the correct order of magnitude for the absolute radiationless-transition rate with the estimated values of the promoting-mode factor. Furthermore, the model worked equally well for all three ordered perovskite compounds considered, and the adjusted ground-state  $t_{2g}$  vibration frequencies are in good agreement with the independently determined values in  $K_2NaGaF_6:Cr^{3+}$  and  $Cs_2NaYCl_6:Cr^{3+}$ .

Comparison of the simulated lineshape functions calculated for  $Cs_2NaYCl_6:Cr^{3+}$  on the single-coordinate linear-coupling model and the two-coordinate quadratic-coupling model in Fig. (5) reveals the source of advantage

Fig. 4. Two-coordinate,  
quadratic-coupling model.

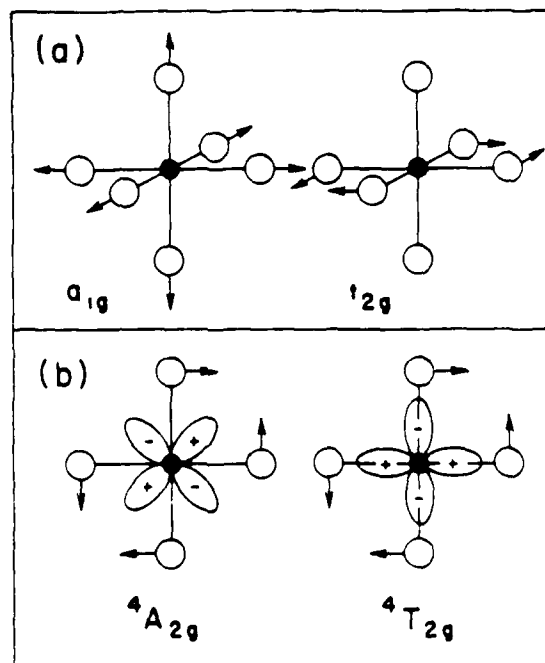
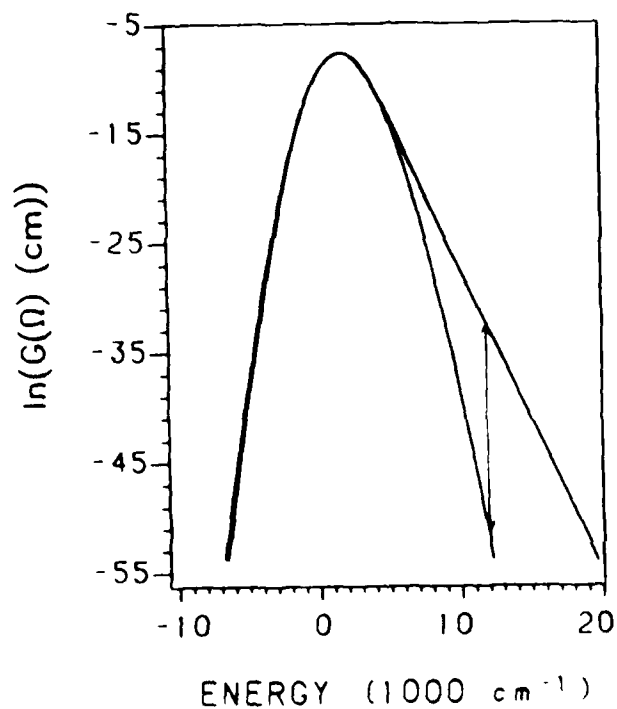


Fig. 5. Comparison of simulated  
lineshapes for single-coordinate,  
linear-coupling model and two-  
coordinate, quadratic-coupling model.



of the latter model. The two lineshapes are virtually indistinguishable over that part of the energy range which is accessible to direct observation, and both are in satisfactory agreement with the measured fluorescence spectrum. However, the two lineshape functions differ by eight orders of magnitude at the gap energy,  $\hbar\Omega_0$ , which accounts for the difference in predicted radiationless transition rate.

#### IV. High-Pressure Photoluminescence

Photoluminescence experiments under intense hydrostatic pressure were undertaken in order to provide systematic control of the physical parameters as an invaluable aid in the development and testing of physical models. Fabrication of a diamond-anvil high-pressure cell according to NBS specifications<sup>20</sup> was initiated at GTE Laboratories and completed at the University of Connecticut. In addition, a special dewar was designed and constructed at the University of Connecticut which permits operation of the diamond-anvil cell at controlled temperatures between +25 and -125°C.

Photoluminescence spectra and lifetimes of  $K_2NaScF_6:Cr^{3+}$  and  $K_2NaGaF_6:Cr^{3+}$  were measured with He-Cd laser excitation at pressures between 0 and 65 kbars and temperatures between 150 and 300 K.<sup>21</sup> In both compounds, a transition from low-field to high-field behavior is evidenced by a pronounced blue shift of the featureless fluorescence spectrum and its ultimate replacement by a highly structured phosphorescence spectrum as shown in Fig. (6). This transition is further attested by an order-of-magnitude increase in radiative lifetime at high pressure. Finally, from its temperature dependence it is evident that the residual fluorescence spectrum at high pressure originates in a thermally populated state.

The observed low-field to high-field transition is attributable primarily

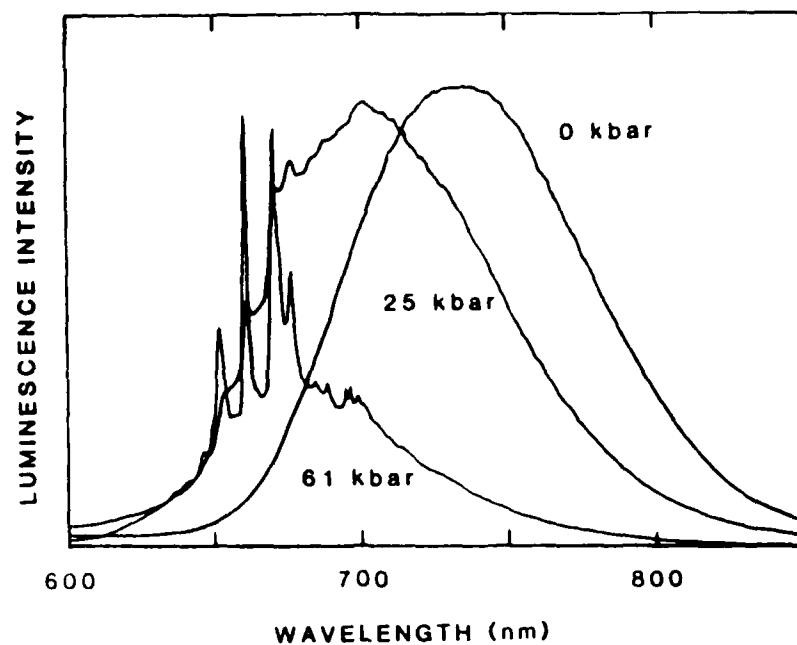
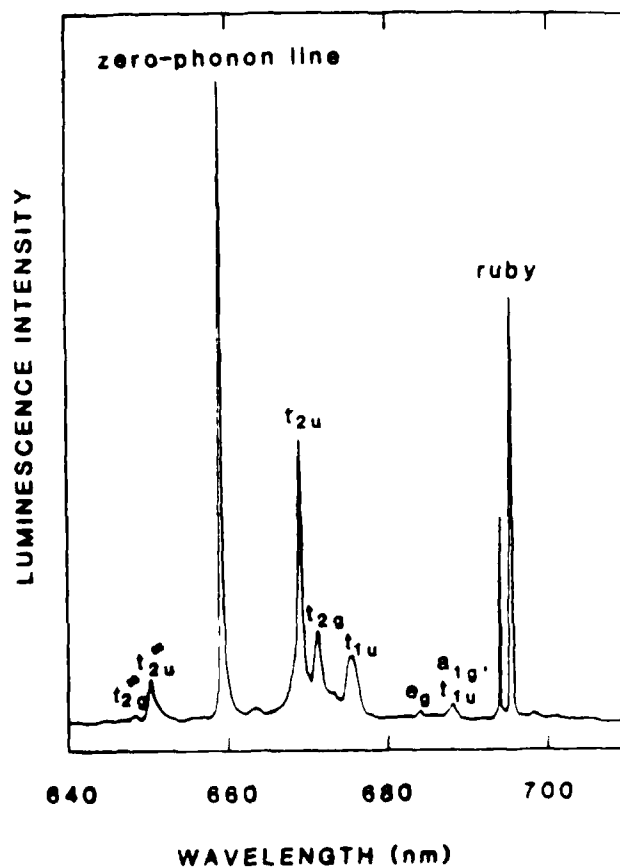


Fig. 6. Pressure-induced low-field to high-field transition in  $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$  at 300 K.

Fig. 7. Photoluminescence spectrum of  $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$  at 61 kbars and  $-119^\circ\text{C}$ . with identification of vibronic structure. Ruby fluorescence measures pressure.



to a substantial pressure-induced enhancement of the crystal-field parameter  $Dq$ , associated with reduction of the lattice parameter. The vibronic structure of the high-pressure, low-temperature phosphorescence spectrum of  $K_2NaGaF_6:Cr^{3+}$ , shown in Fig. (7), which is susceptible to interpretation by analogy with the resolved low-temperature spectrum of the high-field compound  $K_2NaAlF_6:Cr^{3+}$ ,<sup>22</sup> provides quantitative information about the vibration frequencies and electron-lattice coupling at high pressure. There is a 10% increase in vibration frequency at 61 kbar and  $-119^\circ C$ . The pronounced non-linear pressure dependence of  $Dq$  suggests a local-strain effect.

The measured luminescence lifetimes reflect only the change from fluorescence to phosphorescence; thermal quenching was neither expected nor observed in the accessible temperature range. It is evident from Fig. (2) that thermal quenching of fluorescence in the chloride perovskite,  $Cs_2NaYCl_6:Cr^{3+}$ , does occur in the temperature range accessible to our high-pressure apparatus. This material then provides an opportunity to investigate the dependence of activation energy for thermal quenching on the crystal-field parameter  $Dq$  in a single host crystal for comparison with theoretical predictions. However, a number of factors have conspired to impede preliminary measurements: (1) Thermal quenching reduces fluorescence quantum efficiency. (2) Displacement of the emission to longer wavelengths diminishes detector sensitivity. (3) Both He-Cd and He-Ne lasers are poorly matched to absorption bands in this material. (4) The much shorter luminescence lifetimes cannot be measured accurately with a chopped C-W source. Fortunately, these impediments have been removed by acquisition of new equipment in connection with a DoD-University Research Instrumentation Grant, ARO Contract No. DAAG29-85-G-0021. Included in this equipment are a new Argon-ion laser and standing-wave dye laser, a Spex double monochromator and a cooled germanium detector to enhance both sensitivity and

selectivity for spectral measurements, and a pulsed Nd:YAG laser, a LeCroy fast transient digitizer and signal averager and a GaAs photomultiplier for gated-photon-counting lifetime measurements. Both the second harmonic of the Nd:YAG laser and the green line of the argon-ion laser are well matched to the  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  absorption band of  $Cs_2NaYCl_6:Cr^{3+}$ . With this new instrumentation in hand, high-pressure photoluminescence experiments on the chloride elpasolite will have the highest priority. Excitation spectra will also be recorded in order to provide a more complete characterization of the system at high pressure, since it is not feasible to measure optical absorption of materials with such a low extinction coefficient in a diamond-anvil cell.

#### V. Molecular-Cluster Calculations

Semi-empirical molecular-orbital (INDO) cluster calculations have been performed. The cluster for the fluoride elpasolites comprised a central chromium atom, six fluorines, six sodiums and, in some cases, eight potassiums; an analogous cluster was employed for  $Cs_2NaYCl_6:Cr^{3+}$ . Clusters were embedded in an extended point-ion lattice including eight unit cells with fractional surface charges. Both the difference between  $K_2NaScF_6:Cr^{3+}$  and  $K_2NaGaF_6:Cr^{3+}$  and the effects of hydrostatic pressure were simulated by fixing the overall lattice parameter. Only ligand (fluorine or chlorine) displacements were considered, and both  $a_{1g}$  and  $t_{2g}$  vibration frequencies were determined in the  ${}^4A_{2g}$  electronic state. Standard parametrization was employed except for chromium 4s and 4p orbitals, for which an overall scale factor was adjusted to match the measured  $a_{1g}$  vibration frequency; the predicted  $t_{2g}$  frequency at the equilibrium chromium-ligand distance was then in reasonable agreement with experiment as well. However, it was found that this 4s,p scale factor had to be readjusted for each type of ligand and each value of the lattice parameter. Consequently,

the conclusion was reached that the INDO method lacks predictive capability in the present context.

Ab-initio molecular-orbital calculations on much smaller clusters comprising the seven-atom octahedra  $\text{CrF}_6^{3-}$  and  $\text{CrCl}_6^{3-}$ <sup>23</sup> were initiated as well, with a program called MELD.<sup>24</sup> These small-cluster, ab-initio calculations will ultimately be interfaced with lattice-statics calculations.

Preliminary lattice statics calculations have been performed with the HADES III computer program<sup>25</sup> recently acquired from the Atomic Energy Research Establishment, Harwell, England. This program will be modified to remove the restriction to pair potentials, thus permitting incorporation of a molecular cluster, in analogy with the HADESR modification of HADES II written by the principal investigator several years ago. Some of the pair potentials for the surrounding lattice are available from calculations on alkali halides,<sup>26</sup> and others have been calculated at Harwell by the principal investigator, using a combination of the Herman-Skillman atomic structure program<sup>27</sup> and a program called WEDEPOHL, based on an electron-gas model for repulsive potentials. The pair potentials will be adjusted to yield the correct lattice parameter, and the method will be tested on other perovskite compounds with better known properties. The modified HADES III program will be used to calculate symmetrical lattice relaxation in each electronic state in order to establish both the ground-state equilibrium geometry and the strength of coupling to the  $a_{1g}$  mode. Calculations of asymmetrical distortions in orbitally degenerate electronic states (the static Jahn-Teller effect) will also be performed. Of particular interest is the compressibility as a function of hydrostatic pressure, which will be combined with HADES III calculations on the embedded chromium complex as a function of lattice parameter in order to interpret local-strain effects in high-pressure photoluminescence spectra.

Low-field chromium complexes in ordered perovskites are a paradigm for vibronic laser materials based on transition-metal doping of ionic crystals. The reported investigation has helped to identify those factors which control an important loss mechanism, and thus may facilitate formulation of design criteria for such materials.



## PUBLICATIONS

## I. Journal Articles

1. R.H. Bartram and A.M. Stoneham, "Alternative forms for the promoting interaction in radiationless transitions", J. Phys. C: Solid State Phys. 18, L549 -L553 (1985).
2. R.H. Bartram, "Symmetry of point imperfections in solids", Journal of Computers and Mathematics with Applications (in press).
3. J.F. Dolan, L.A. Kappers and R.H. Bartram, "Pressure and temperature dependence of chromium photoluminescence in  $K_2NaGaF_6:Cr^{3+}$ ", submitted to Physical Review Letters.
4. L.J. Andrews, A. Lempicki, B.C. McCollum, C.J. Giunta, R.H. Bartram and J.F. Dolan, "Thermal quenching of chromium photoluminescence in ordered perovskites. I: temperature dependence of spectra and lifetimes", submitted to Physical Review B.
5. R.H. Bartram, J.C. Charpie, L.J. Andrews and A. Lempicki, "Thermal quenching of chromium luminescence in ordered perovskites. II: theoretical models", submitted to Physical Review B.

## II. Papers Presented at Meetings

1. R.H. Bartram, J.C. Charpie, L.J. Andrews and B.C. McCollum, "Mechanism of fluorescence quenching in low-field chromium complexes", Bull. Am. Phys. Soc. 29, 538 (1984).
2. R.H. Bartram, "Theory of fluorescence quenching in low-field chromium complexes in solids", in Tunable Solid State Lasers, Eds. P. Hammerling, A.B. Budgor and A. Pinto (Springer-Verlag), Berlin and Heidelberg, 1985) pp. 155-163 (Invited paper presented at First Annual Conference on Tunable Solid State Lasers, LaJolla, California, 13-15 June, 1984).
3. R.H. Bartram, J.C. Charpie, J.F. Dolan, L.J. Andrews and B.C. McCollum, "Mechanism of fluorescence quenching in low-field chromium complexes" (Contributed paper presented at International Conference on Defects in Insulating Crystals, Salt Lake City, Utah, 20-24 August, 1984).
4. J.F. Dolan, L.A. Kappers, R.H. Bartram and L.J. Andrews, "Pressure dependence of chromium photoluminescence in ordered perovskites", Bull. Am. Phys. Soc. 30, 420 (1985).
5. J.F. Dolan, L.A. Kappers, R.H. Bartram and L.J. Andrews, "Pressure and temperature dependence of chromium photoluminescence in ordered perovskites", Bull. Am. Phys. Soc. 30, 1135 (1985).
6. R.H. Bartram, "Pressure and temperature dependence of chromium photoluminescence in ordered perovskites" (Invited paper presented at Topical Meeting on Tunable Solid-State Lasers, Arlington, Virginia, 16-17 May, 1985).

## SCIENTIFIC PERSONNEL

### I. Senior Personnel Supported

1. Professor Ralph H. Bartram (Principal Investigator)
2. Associate Professor Lawrence A. Kappers (Physics, U. Conn.)
3. Associate Professor Angelo R. Rossi (Chemistry, U. Conn.)
4. Professor Dr. Johann-Martin Spaeth (Physics, Universitat-Gesamthochschule Paderborn, W. Germany)

### II. Graduate Students Supported

1. Theodore Fischer
2. James F. Dolan (Ph.D. Thesis in preparation)
3. John C. Charpie
4. Andrew Rinzler
5. Robert Wein

### III. Unsupported Research Collaborators

1. Professor Alexander Lempicki (Chemistry, Boston University)
2. Dr. Leonard J. Andrews (GTE Laboratories, Waltham, MA)
3. Dr. B.C. McCollum (GTE Laboratories, Waltham, MA)
4. Dr. A.M. Stoneham (Theoretical Physics, AERE Harwell, England)
5. Associate Professor Douglas S. Hamilton (Physics, U. Conn.)

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